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Investigation of the Kinetics of
Crystallization of Molten Binary
and Ternary Oxide Systems

Quarterly Status Report No. 5

Contract NASW-1301

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Investigation of the Kinetics of Crystallization of

Molten Binary and Ternary Oxide Systems

Quarterly Status Report No. 5 - September 1, 1966 through November 30, 1966

Contract No. NASW-1301

SUMMARY

Terms of the first contract extension are such as to allow an increased effort in this research area as well as to make possible several innovations in procedures carried out during the fifth quarter. A small micro-furnace for direct use under a microscope was constructed and used to study nucleation and crystal growth rates. An enlarged platform furnace useable in air at temperatures up to 1800 C was built for fiberizability research. Equipment was constructed for the dynamic evaluation of the bulk modulus of experimental glasses. Previously established research procedures for the preparation of new experimental glasses, the measurement of the viscosity of these glasses, and the determination of their Young's modulus were continued.

Capital equipment available to the program was supplemented by the UACRL purchase of apparatus suitable for melting and casting high temperature glasses in vacuum or in chosen inert atmospheres. Delivery of this equipment is scheduled for mid-March of this year.

Near the end of the fifth quarter an experimental glass was devised which had excellent fiberizing characteristics and whose hand-drawn fiber samples gave values for Young's modulus on eleven occasions ranging from 20 to 27 million psi with variation in heat treatment. However, a limited number of subsequent experiments possible with this glass before this report had to be written have given only lower values of Young's modulus. It is not known at this time, therefore, whether the initial high values are due to the precise state of oxidation equilibrium present in the glass (which contains a constituent that can exist in several states of oxidation), or the exact heat treatment accumulated by the bulk glass before the

fiber is pulled. The methods of testing employed have been critically analyzed and all known errors would give too low a value for Young's modulus instead of too high with the single exception of pronounced ellipticity in the fiber. Since the original test fibers were destroyed before an examination for ellipticity was carried out and since none of the subsequent fibers are elliptical, this hypothesis can neither be refuted or confirmed as yet.

INTRODUCTION

This is the fifth quarterly status report for Contract NASW-1301 entitled, "Investigation of the Kinetics of Crystallization of Molten Binary and Ternary Oxide Systems." This fifth quarter of the contract, which incidently is also the first quarter of the expanded contract, started September 1, 1966 and extended to November 30, 1966. The primary objective of this program is to gain a better understanding of the essentials of glass formation by measuring the rate at which crystallization occurs and the effects of anti-nucleating agents on the observed crystallization rate for systems which tend to form complex three dimensional structures. Determination of the crystallization rate is carried out by continuously measuring the viscosity and electrical conductivity of the molten system as a function of time and temperature with checks of surface tension at selected temperatures. In this period an important supplementary method for determining the crystallization rate, namely direct microscopic examination of samples in a micro-furnace has been introduced and has proven to be very helpful. Glass formation in this research is, therefore, regarded as a rate phenomenon where the probability of such glass formation is greatly increased by employing cooling rates high enough to defeat the formation of the complex many-atom three-dimensional molecule. This view of glass formation justifies the consideration of oxide systems previously thought impractical and allows the search for systems which may yield high strength, high modulus glass fibers to be carried out on an unusually broad basis.

Preparation of Glass Systems for Preliminary Examination

Twenty-six new glass batches were formulated, mixed and melted in the fifth quarterly period along with new preparations of twenty-two older glass formulations to provide additional material for property evaluation. Thirteen of the new glass preparations were based on calcia-alumina as the glass formers together with extensive modifications and additions. The other thirteen new glasses were silica-alumina "invert" glasses and silica-yttria "invert" glasses with extensive variations. As will be recalled from several of the earlier quarterly reports on this contract, these "invert" glasses were developed by Stevels (Ref. 1) and may contain as little as 34 mol % silica. The composition of such glasses is indicated by a parameter Y designating the average number of bridging ions per SiO_4 tetrahedron and calculated from the expression

$$Y = 6 - \frac{200}{P} \quad \text{where} \quad P = \text{mol \% } SiO_2$$

so that when P = 33-1/3, Y = 0 and the SiO_4 groups are isolated; when P = 40%, Y = 1 and on the average SiO_4 groups appear in pairs. Properties of these glasses such as viscosity at a given temperature, the viscosity activation energy, thermal expansivity, electrical deformation loss go through extreme values when the parameter Y passes through the value of 2.0. There is every reason, therefore, to believe that mechanical properties such as Young's modulus will show a similar parabolic relationship when plotted against the parameter Y, climbing steeply as Y decreases from 2 to 1 and then falling off again.

Procedures for Characterizing Glass Systems Investigated and the Results Obtained

The kinetics of crystallization of the glass systems investigated under this contract are determined from continuous measurement of the electrical resistivity and viscosity of the system and by direct microscopic observation of the behavior of the glass batch of various temperatures using a recently constructed micro-furnace. These measurements plus the measurement of Young's modulus of the bulk glass at room temperature serve to help characterize the system studied. In addition recently completed equipment is available for measuring shear modulus of the bulk glass so that together with the measurement of Young's modulus Poisson's ratio can be determined. Finally, characterization of the molten oxide system is completed by determination of their glass forming and fiberization qualities and by measurement of Young's modulus and ultimate tensile strength on the hand-drawn fibers produced in the fiberization research.

Many of these procedures have been described in detail in our previous quarterly and summary reports. In this quarterly report, therefore, emphasis is placed on the equipment used for optical studies of crystallization, the method of measuring shear modulus, and the special furnace constructed for fiberization research.

Micro-Furnace for Optical Studies of the Kinetics of Crystallization

The UACRL micro-furnace design owes much to the earlier furnace constructed by Morley (Ref. 2) for exactly the same type research, namely, the study of crystallization kinetics in molten glass. The micro-furnace consists essentially of a platinum-10% rhodium tube, 0.250 in. O.D. and with a wall thickness of 3 mils, which is damped between the two copper bars (0.125 in. x 0.500 in.). A circular shelf of platinum is welded to the inside of the tube, and the crucible is placed in a 0.128 in. hole in this shelf. Crucibles are fabricated by cutting platinum tubing (0.125 in. dia with 5 mil wall thickness) into pieces 0.065 in. long and then pressing them in a die so that they form a 40 degree included angle.

Figure 1 shows the micro-furnace without radiation shielding. Subsequently radiation shielding was found necessary and was added by welding two rings of 0.057 in. Kathal wire to the nichrome plates at the two ends of the heater tube. An inner shield of 4 mil platinum-rhodium sheet and an outer shield of 5 mil nichrome sheet were welded to the inner nichrome wire ring that is on the lower nichrome plate. Two 5 mil nichrome shields were welded to the outer nichrome wire ring on the upper circular nichrome plate.

Figure 1 also shows the 1/8 in. diameter copper tubing which is used to supply water-cooling to the copper electrical connectors. The power supplied the furnace comes from a filament transformer of 0.975 KVA capacity and a 20 ampere Variac. To attain a temperature of 1400 C a current of 140 amperes at 1.1 volts (60 cycle a-c) has proven adequate.

The entire experimental arrangement with the exception of the power supply is shown in Fig. 2. It comprises the micro-furnace, microscope and camera, micro-manipulator used to weld and position the thermocouple, the x-y recorder used for plotting time-temperature response of the furnace, and the 3 mil platinum-platinum 10% rhodium thermocouple carefully positioned in the center of the furnace. Experience has shown that the furnace temperature can be maintained to within $\pm$ 4 C at 1250 C.

In actual use, the crucible is inserted into the furnace, a large fragment of glass is placed in the crucible and the crucible then heated. Smaller glass fragments are later added to completely fill the crucible. The glass is then heated until all of the bubbles disappear and then cooled to the temperature selected for crystal growth observation. The thermocouple is then lowered into the melt and photographs are taken of the crystals growing on the thermocouple at selected time intervals. Seed crystals can be grown on the thermocouple by placing it in the melt and then withdrawing it to a cooler part of the furnace. A step that may or may not be necessary depending on the composition of the glass under investigation. High-speed film is used (Polaroid-ASA 3000) and good quality pictures are readily obtainable. The actual sizes of the crystals in the photographs can readily be obtained by calibrating the optical system employed.

Kinetics of Crystallization Studied by Viscosity and Electrical Resistivity

Procedures

No changes have been made in either of these methods during the fifth period. At the time of compilation of this report viscosity-temperature curves have been obtained for glass batches 1, 24, 25, 29, 30, 31, 32, 41, 43, 45, 46, 48, 49, 50, 52, 63-2, 64, 65 66, 68, 69, 71, 72, 73 and 75. This represents an increase from 16 to 25 in this period.

Sonic Determination of Young's Modulus for Bulk Glasses

The equipment described in the fourth quarterly report (Ref. 3) has been used to measure the dynamic Young's modulus for seven additional glass batches. The values measured ranged from 10.2 million psi to 16.5 million psi.

Shear Modulus of Bulk Glass Samples Determined by Sonic Measurements

The basis of the experimental program on the kinetics of crystallization of molten binary and ternary oxides has been the assembling of these oxides in such proportions that if they were allowed to crystallize, they would yield complex three-dimensional ring structures. It is possible, therefore, that the glasses formed from such melts may show anisotropy. The purpose of measuring both Young's modulus and the shear modulus of the bulk glasses is to determine Poisson's ratio and, consequently, any attendant evidence of anisotropy.

To measure the shear modulus of the bulk glass, small piezoelectric crystals are bonded to each end of the specimen under test. One of the crystals is then selected as the transmitter and driven with a short burst of radio-frequency electrical energy. The pulse is transmitted through the specimen and received by the second piezoelectric crystal bonded to the far end of the specimen. This receiving crystal which is identical to the transmitting crystal is mechanically excited by the compressional waves traveling down the glass bar. The time delay between the transmitted and received pulse is then measured on a duel beam oscilloscope and/or an E-put meter. The velocity of this sound wave and the resulting value for the shear modulus of the specimen are then calculated.

In this period, the new circuitry has been tested on standard glasses such as fused silica and has given satisfactory values for Poisson's ratio. In the sixth quarter it will be used to investigate the anisotropy of the experimental glasses.

Evaluation of Glass Forming Characteristics and Fiberizability

Oxide materials previously melted in the standard kilns using the procedures described earlier in this report furnish the starting materials used in this phase of our research. From the previous firing in the kiln they have emerged either as fully melted glasses, glass and crystalline masses, or materials that appear similar to clinkers or cinders. One chooses a sufficient amount of this material to fill a 15 milliter platinum crucible. The material is then crushed or ground to approximately 10 mesh size and placed in the platinum crucible. The platinum crucible then takes the place of the large alumina crucible pictured (Figure 3) on the motor-driven platform of the Super-Kanthal hairpin furnace (Figure 3). The furnace platform is then raised rapidly until the crucible is in the center of the furnace, which has previously been heated to the desired temperature. The crucible is then kept at the desired temperature for a time varying from one-half hour to two hours dependent on the particular glass under investigation and is then lowered as rapidly as possible. As soon as the crucible becomes accessible, one man picks it up in tongs and a second man dips a twenty mil platinum wire into the molten glass and runs away from the crucible as rapidly as possible. Usually in this manner, it is possible to hand draw a glass fiber 2 to 5 mils in diameter and thirty to forty feet long. The platinum wire is, of course, mounted in a glass tubing handle. In this simple fashion, it is readily possible to obtain crude ideas of the glass forming characteristics and fiberizability of the various glass batches at a variety of temperatures. The Super-Kanthal kiln using experimental types Super-Kanthal hairpin elements readily obtains a temperature of 1800 C in air.

Young's Modulus Measurements on Hand-Drawn Glass Fibers

In studying the properties of the research glasses in fiber form the most important single parameter is probably Young's modulus of elasticity. In Figure 4 the apparatus used for the measurement of the tensile modulus of the experimental hand-drawn glass fibers is shown. An x-y plotter records load versus crosshead movement so that with the calibration of the load cell established, the corrections in the output of the linear variable differential transformer known (LVDT), and the pertinent physical dimensions of length and diameter measured; it is possible to read stress, strain, and Young's modulus as the slope from the recorder tracing. The device for straining the glass fiber is shown separately in Fig. 5 where A is the loading jaw for the fiber, B is a strain gage for determining loads on the fiber, and C is the linear variable differential transformer, the motion of whose core causes the electrical signal measuring the strain, D is the micrometer for correlating the motion of the transformer core with electrical output, and E is the constant speed loading motor for applying the strain. Six inch gage lengths or greater are used for all tests.

The data obtained for the experimental glass AB is shown in Fig. 6. Here the values of Young's modulus range from 20 million psi to 27 million psi as plotted against fiber diameter in mils (thousandths of an inch). This variation in the modulus is not a size effect, however, but is actually a variation with effective heat treatment since the smaller diameter fibers cool more rapidly as has been convincingly demonstrated earlier research (Ref. 4). The values used for this graph were all obtained from a given batch of glass AB which had initially been prepared at 1500 C and then briefly held at 1620 C before the fiber was hand-drawn from the batch. Subsequent experiments where the batch was held at 1620 C for longer periods invariably gave much lower modulus values ranging from 16.5 million psi to 12.2 million psi. Since this particular glass contains a constituent whose state of oxidation can be variable, it is felt at this time that this decrease in Young's modulus is due to a change in the oxidation equilibrium present in the glass. All known errors in modulus determination yield low values not high with the single possibility of pronounced ellipticity in the fiber and this will be investigated as soon as a new glass batch can be prepared and measured since no glass fibers remain from the original lot.

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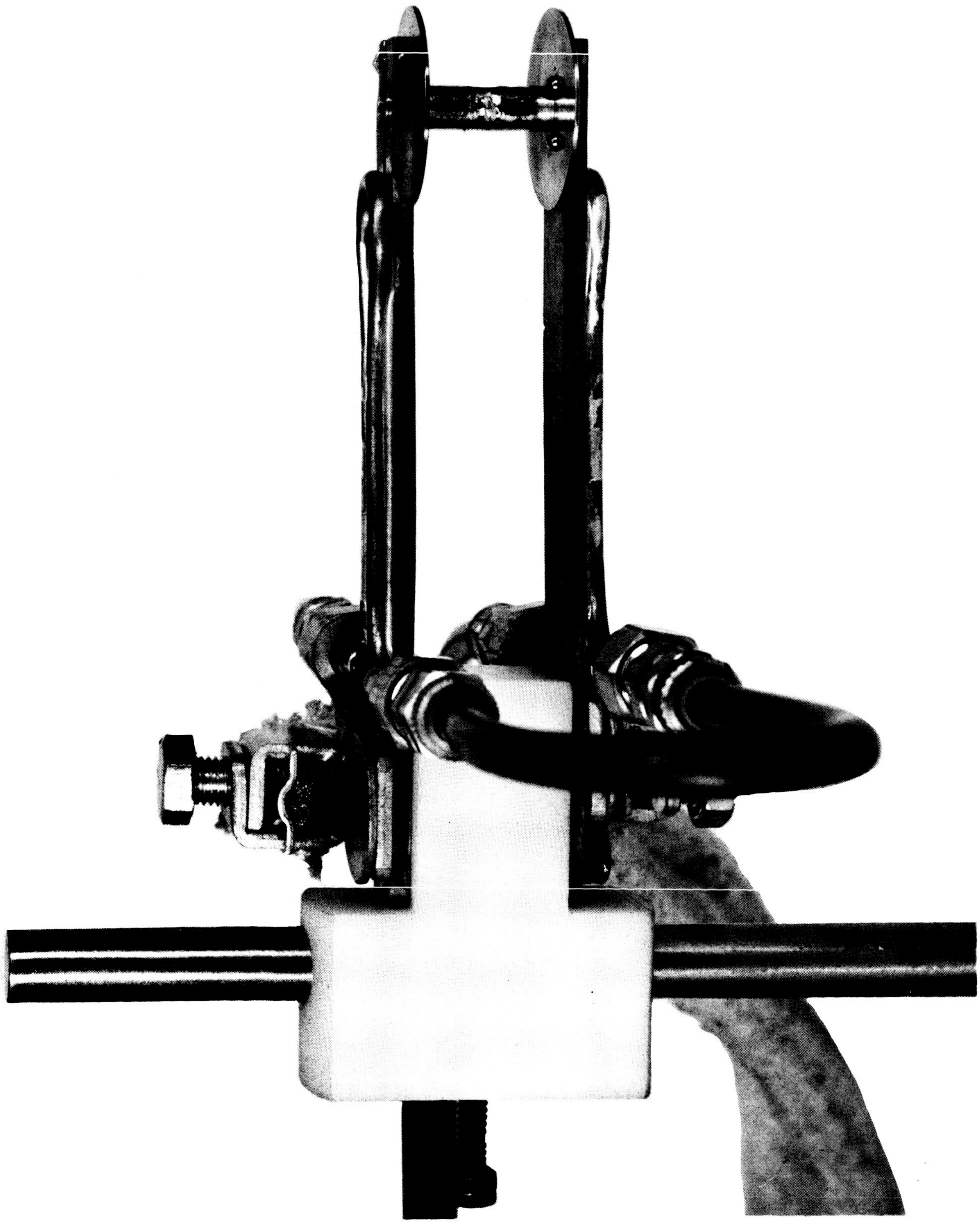

CLOSE-UP OF MICRO-FURNACE. HEAT SHIELDS REMOVED

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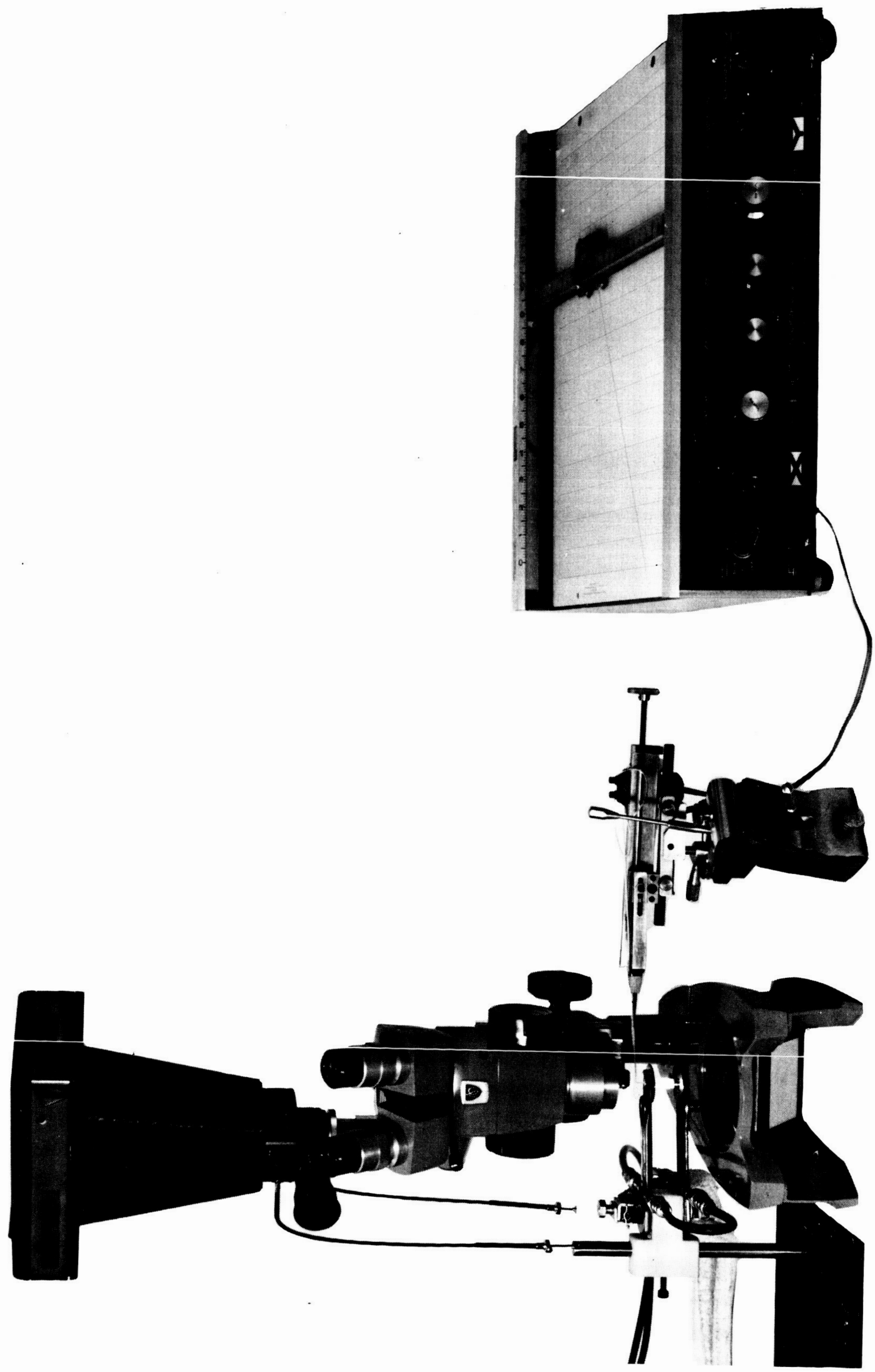
FIG 2

MICRO-FURNACE IN POSITION FOR USE, AND ASSOCIATED EQUIPMENT



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IMPROVED PLATFORM KILN

FIG. 4

COMPLETE TENSILE-MODULUS APPARATUS

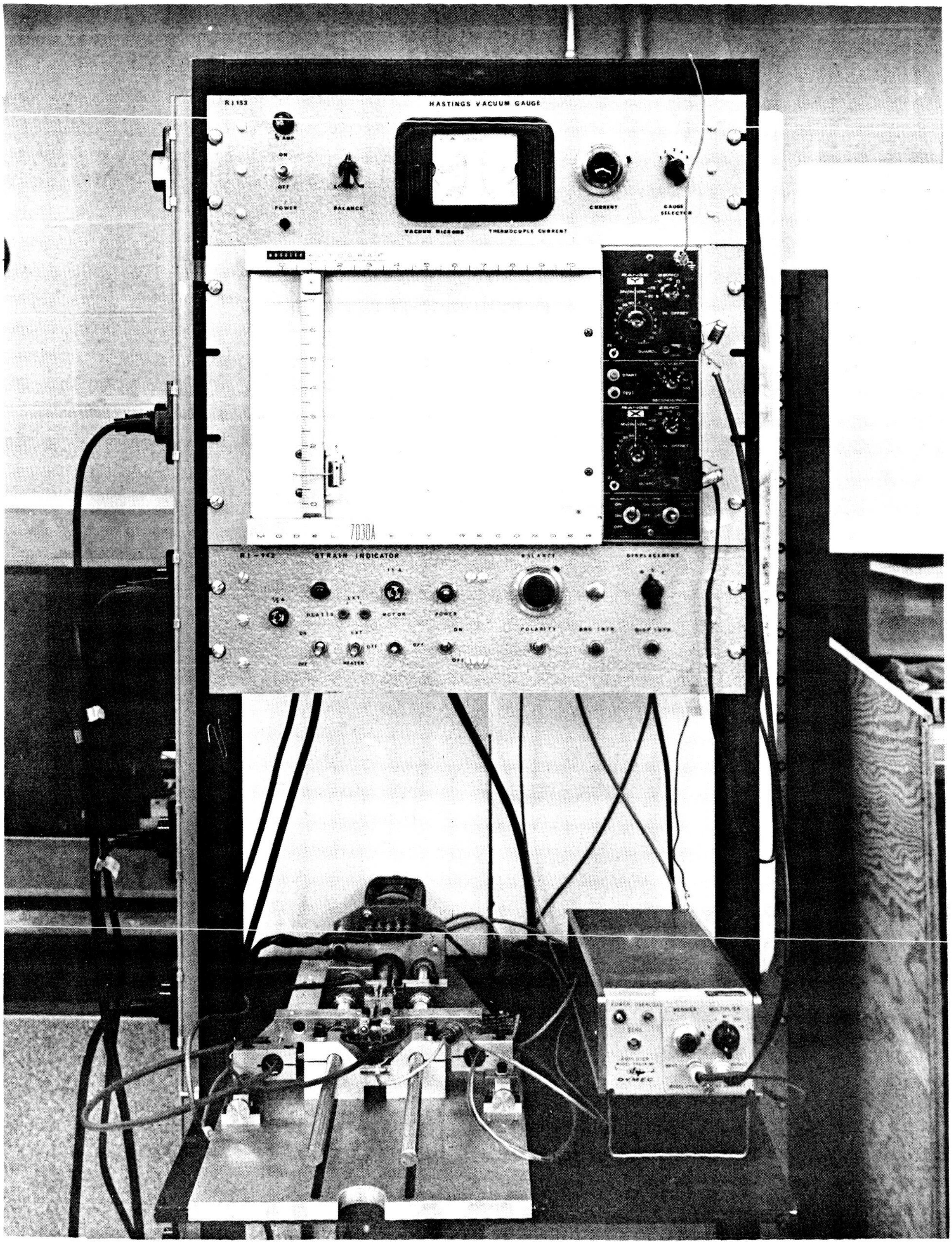
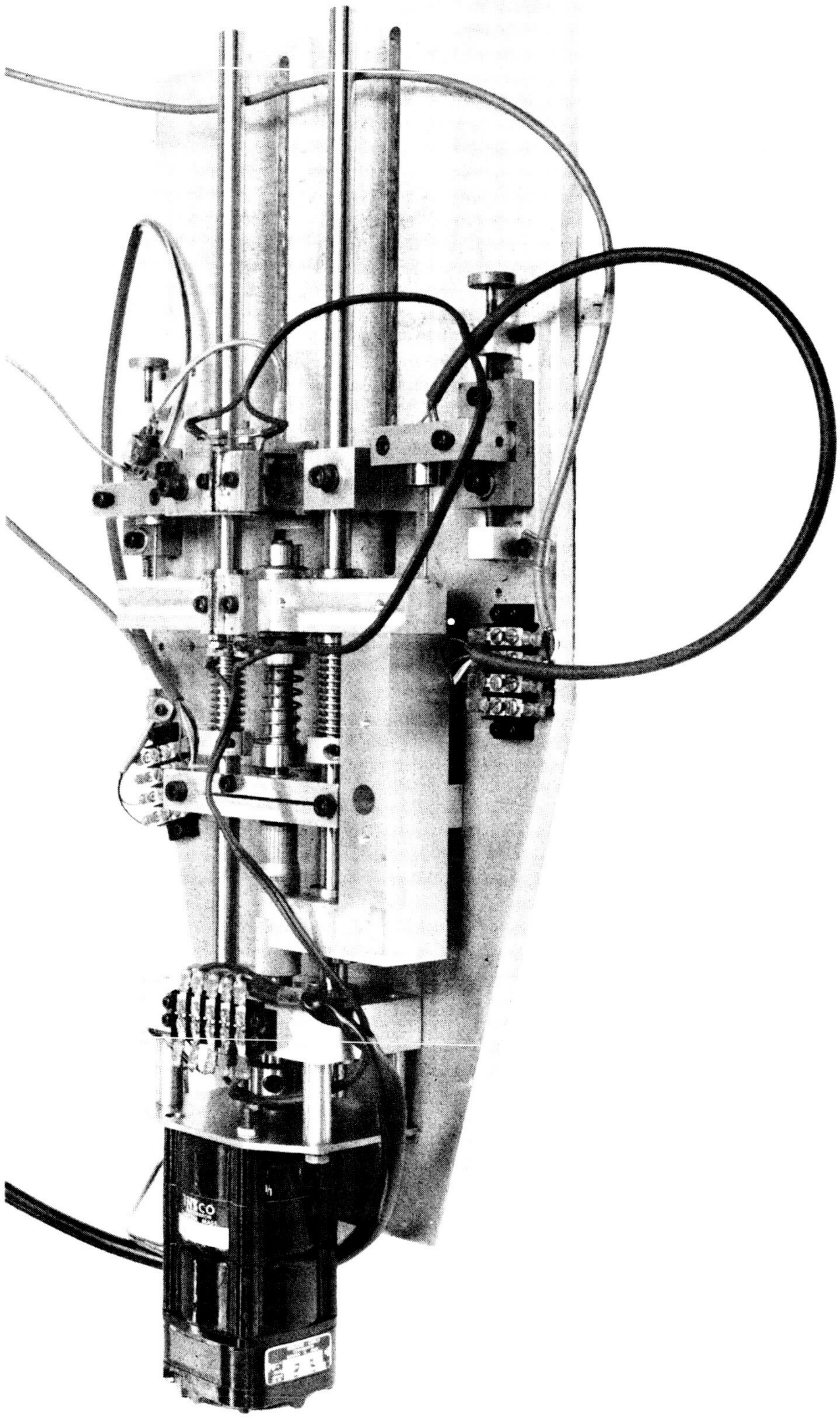


FIG. 5



TENSILE - MODULUS TESTER

EFFECT OF HEAT TREATMENT ON MEASURED VALUES OF YOUNG'S MODULUS FOR EXPERIMENTAL GLASS BATCH AB